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VAPOR-PHASE OXIDATION AND SPONTANEOUS IGNITION -

CORRELATION AND EFFECT OF VARIABLES

By Donald E. Swarts and Milton Orchin

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SUMMARY

The spontaneous ignition temperatures of eight structurally different hydrocarbons were determined and correlated with the behavior of the same hydrocarbons toward vapor-phase oxidation. Since good correlation of the two phenomena was obtained, it is likely that similar oxidative mechanisms are operative in both.

Studies with methylcyclohexane show that there is an apparent zone of decreasing oxidation with increasing temperature. This zone corresponds to the range of nonignition found in spontaneous-ignition-temperature work and lends further support to the validity of the concept of separate high- and low-temperature oxidation mechanisms. The studies also show that the extent of oxidation decreases as the stoichiometry is reduced.

Cyclic hydrocarbons have greater resistivity to preflame combustion than either a straight-chain olefin or the straight-chain paraffin of the same number of carbon atoms. The order of decreasing resistance to oxidative attack for the hydrocarbon structures tested is aromatic > branched paraffin > cyclic paraffin > straight-chain olefin > straight-chain paraffin.

The spontaneous ignition temperature of an organic compound is shown to be greatly affected by variables such as surface-volume (S/V) ratio, fuel-oxygen (HC/O_2) ratio, and pressure. The spontaneous ignition temperature appears to vary linearly with the S/V ratio of the ignition chamber used for the determination. Observations of the physical variables affecting spontaneous ignition temperatures indicate that no spontaneous ignition temperature reported in the literature can be regarded as the lowest possible spontaneous ignition temperature and that the conditions necessary to approach the absolute spontaneous ignition temperature, a theoretical value, are a low S/V ratio, higher-than-atmospheric pressures, and an optimum fuel-oxygen ratio. Surface models, with spontaneous ignition temperature, S/V ratio, and pressure as coordinates, at various fuel-oxygen ratios depict important fundamental findings on vapor-phase-oxidation behavior.

INTRODUCTION

Earlier work on spontaneous-ignition-temperature determinations (ref. 1) showed a definite correlation between the observed spontaneous ignition temperature of a compound and its chemical structure. The effect of increased branching on a hydrocarbon was to raise the spontaneous ignition temperature, whereas increasing the length of the uninterrupted methylene chain lowered the spontaneous ignition temperature. In addition, the spontaneous ignition temperature was correlated with the number of 1^0, 2^0, and 3^0 hydrogen atoms. From this considerable amount of data, it was possible to predict with fair accuracy the spontaneous ignition temperature of a given hydrocarbon structure in the particular ignition apparatus employed. Other investigations have reported different spontaneous ignition temperatures for the same compound using different conditions of stoichiometry and pressure in various types and sizes of ignition vessels. There is considerable disagreement about what constitutues the "minimum" ignition temperature of a compound and about the factors which effect the spontaneous ignition temperature. Studies on all the physical and chemical variables which influence the spontaneous ignition temperature have been lacking and no standard method for determining the most useful and meaningful spontaneous-ignition-temperature value of an organic compound has been accepted. Although the spontaneous ignition temperature has no obvious relation to the flash and fire points, there is excellent correlation with the octane rating of hydrocarbons and with their critical compression ratios.

The present work on the behavior of hydrocarbons under preflame vapor-phase-oxidation conditions has indicated the importance of chemical structure and, since spontaneous-ignition-temperature behavior is also structure dependent, a correlation between the spontaneous ignition temperature and the behavior to preflame oxidation might be expected. A qualitative dependence has indeed been found. It is evident that the spontaneous ignition temperature can be a very useful tool in predicting the behavior of a hydrocarbon toward oxidative attack and preignition in other combustion processes. The difference in the nature of the combustion products obtained as the temperature is varied from 200^0 to 500^0 C lends additional support to the concept of separate high- and low-temperature mechanisms. The nonignition zone so often observed between approximately 300^0 and 400^0 C in spontaneous ignition temperature determinations has its counterpart in the behavior toward vapor-phase oxidation of methylcyclohexane. Important variables such as surface-volume ratio, hydrocarbon-oxygen ratio, and pressure affect the spontaneous ignition temperature and an effort has been made to define better spontaneous ignition limits and to describe what constitutes a minimum ignition temperature.

This investigation was conducted at the University of Cincinnati under the sponsorship and with the financial assistance of the National Advisory Committee for Aeronautics.

DESCRIPTION OF APPARATUS AND PROCEDURE

Spontaneous Ignition Temperatures

The apparatus used to determine spontaneous ignition temperatures was constructed and used previously in this laboratory and is described in reference 1. It consists essentially of a 43-cubic-centimeter, cylindrical, electrically heated, stainless-steel cup. The temperature is measured potentiometrically with a thermocouple and the fuel-air ratio is varied by a regulated flow of preheated air. An air-flow rate of 125 cc/min is used throughout all of the work. The hydrocarbon to be tested is added dropwise at intervals by a hypodermic syringe or a medicine dropper as the cup and furnace cool. The temperature below which no further ignition is observed is defined as spontaneous ignition temperature of the hydrocarbon at an air flow of 125 cc/min. Since the fuels tested are quite volatile, spray-injection procedures have not been employed. As a check for these determinations, the spontaneous ignition temperature of isooctane found previously (515° C at 125 cc/min) has been duplicated to within 1° C.

Vapor-Phase Oxidation in Reactor Tubes

The apparatus employed in the reactor-tube experiments for controlled oxidation is similar to that described in reference 2, with modifications to permit a variation of stoichiometry of the charged gaseous mixture as desired. The three main units of the apparatus are (1) the hydrocarbon-oxygen-nitrogen mixing tube, (2) the oxidation chamber, consisting of a 1/16-inch-inside-diameter by 13-inch-long glass tube in an electrically heated furnace, and (3) cold traps (-70° C) for rapid quenching of the reaction products. An alcoholic solution of 2,4-dinitrophenylhydrazine is used in a final scrubber to trap any volatile carbonyl compounds.

Tank oxygen and tank nitrogen are dried by passing them through separate columns of Drierite and are conducted through separate calibrated flowmeters to a mixing tube. In the mixing tube the oxygen and nitrogen are thoroughly mixed by turbulent flow through 6 inches of packed glass helices. This gaseous mixture is then bubbled through the hydrocarbon which is held at a constant temperature by a vapor bath in order to secure a known fuel-oxygen-nitrogen mixture. The ratio of oxygen to nitrogen is varied to obtain 1, 1/5, 1/10, or 1/20 stoichiometric mixtures of fuel and oxygen as desired. The fuel-oxygen-nitrogen mixture is then passed through

the reaction chamber at a selected contact time and temperature and the reaction products are quenched in cold traps. Since noncondensing gases or aerosols are produced in experiments with methylcyclohexane, the second trap is loosely packed with glass wool to trap these products. The oxidation products are analyzed for total peroxide, hydrogen peroxide, and acids as outlined in reference 3. A solution of bromine in carbon tetrachloride is used to test for olefins in the organic portion of the products. The refractive index is also measured. Quantitative tests are made for total carbonyl and aldehydes.

RESULTS AND DISCUSSION

Oxidation of Hydrocarbons

Toluene.- The data from the vapor-phase oxidation of toluene are shown in table I. A stoichiometric toluene-oxygen mixture was reacted at 550° C and at contact times of 0.16 and 0.64 second. As can be seen from table I, there is little or no appreciable oxidation occurring with toluene under these conditions. This resistivity to oxidation is characteristic of the aromatic compounds, and the small amount of products formed undoubtedly arise from attack on the methyl hydrogen atoms (ref. 2). The relatively greater quantities of hydrogen peroxides and hydroperoxides are in agreement with the oxidation behavior of other hydrocarbons, such as isooctane and isobutane which also contain mostly 1° hydrogen atoms and which are attacked by oxygen only at higher temperatures.

Methylcyclohexane.- Data pertaining to the vapor-phase oxidation of methylcyclohexane are shown in tables II and III. The stoichiometry of the hydrocarbon-oxygen-nitrogen mixture (calculated on the basis of the complete oxidation of methylcyclohexane) was varied from 1 to 1/20 over a range of temperatures from 350° to 550° C at 50° intervals. The contact time in all the experiments was 0.16 second. At 350° C there is no observable reaction, while at 400° C the rate of reaction is relatively large. Since there was some question as to whether control of reaction rate could be maintained upon raising the temperature another 50° to 100° C, the stoichiometry of the gaseous mixture was reduced to 1/10 and the oxidations were carried out at five different temperatures, ranging from 350° to 550° C (table II, 0.1 stoichiometric quantities). The maximum yield of oxidation products occurs at 400° C, with decreased yields at 450° and 500° C and with another rise in yields starting at approximately 550° C. At first, it might seem anomalous that, with other factors remaining unchanged, the product yield decreases with an increase in temperature. However, as was pointed out in previous work on hydrocarbon ignition (ref. 1), many hydrocarbons which undergo spontaneous ignition in the low-temperature region exhibit an intermediate zone of nonignition between the low- and high-temperature ranges. Methylcyclohexane has a spontaneous

ignition temperature of 323° C and consequently may show such a nonignition region under certain conditions. The lesser amounts of oxidation products observed at 450° and 500° C may well correspond to this region, that is, a zone where the predominant influence of the low-temperature oxidation mechanism has begun to fade and that of the high-temperature mechanism has not yet become effective. With a reaction tube of $1\frac{1}{4}$-inch inside diameter and contact time of 10 to 13 seconds (ref. 4), this maximum occurs near 325° C, or about 75° lower than that observed with the 1/16-inch-inside-diameter tube. This difference of 75° illustrates the importance of a high surface-volume ratio in controlling chain-branching reactions.

The effect of changing the stoichiometry is demonstrated by the data in tables II and III which show that the extent of oxidation decreases with a reduction in stoichiometry. No organic peroxides were observed in any of these experiments. Qualitative tests for total carbonyl compounds and aldehydes were positive for all experiments in which the temperature exceeded 350° C.

Effect of Structure on Spontaneous Ignition Temperatures

and on Vapor-Phase Oxidation

The spontaneous ignition temperatures were determined for eight hydrocarbons. These compounds were chosen to cover a wide range of structural types, and the spontaneous-ignition-temperature values are shown in table IV. The spontaneous ignition temperatures of toluene, isooctane, and n-heptane were determined in this laboratory and reported in reference 1. The compounds n-heptane and 3-heptene have spontaneous-ignition-temperature values in the low-temperature range, methylcyclohexane has an intermediate value, and 2,2,5-trimethylhexane, 2,3-dimethylbutane, isooctane, 2,2-dimethylbutane, and toluene have spontaneous-ignition-temperature values in the high-temperature range. The behavior of the same hydrocarbons to controlled vapor-phase-oxidation experiments in the following system is shown in table V. Judged by the amounts of oxidation products, the resistance to vapor-phase oxidation shows the same general order for the compounds tested as obtained for the spontaneous ignition temperature, with some doubt as to the exact order of 2,2-dimethylbutane, isooctane, and 2,3-dimethylbutane. At 350° C and 0.04-second contact time, 3-heptene yields only about one-third as much product as n-heptane (compare runs 10 and 9), while methylcyclohexane at 350° C and 0.16 second shows no attack (run 8). However, at 400° C and 0.16 second, methylcyclohexane is oxidized to a much greater extent than 2,2,5-trimethylhexane at 450° C and 0.16 second (compare runs 7 and 6). Similarly, 2,2,5-trimethylhexane at 550° C and 0.08 second is more readily attacked than 2,3-dimethylbutane, isooctane, or 2,2-dimethylbutane at 0.08 second and 500°, 550°, and 500° C, respectively (compare run 5 with runs 4, 3, and 2). Toluene at 550° C and 0.16 second (run 1) is oxidized least of all. The difference in susceptibility to oxidation of

2,3-dimethylbutane, isooctane, and 2,2-dimethylbutane is slight and, since no comparable run of isooctane at 500° C and 0.08 second is available for a better comparison, the exact order of resistance to oxidation is difficult to evaluate.

Considering only 2,3-dimethylbutane and 2,2-dimethylbutane the greater ease of oxidation of 2,2-dimethylbutane compared with the 2,3-isomer is the reverse of their respective spontaneous-ignition-temperature values. However, the spontaneous-ignition-temperature determinations were made in air (approximately 20 percent oxygen), while runs in the reactor tube were made using pure oxygen. As will be discussed in a later section, the hydrocarbon-oxygen ratio is quite important in oxidation experiments. It has been shown (ref. 5) that, in spontaneous-ignition-temperature determinations using pure oxygen, the order is reversed; that is, 2,3-dimethylbutane has a higher spontaneous ignition temperature than isooctane which, in turn, has a higher spontaneous ignition temperature than 2,2-dimethylbutane. These spontaneous ignition temperatures are near 300° C which is the region of the low-temperature oxidation mechanism. Those in air are near 500° C and ignite via the high-temperature mechanism. Seemingly, the same structural differences which are important and which determine selectivity at low temperatures are of lesser importance at high temperatures. The effect of stoichiometry and structure on spontaneous ignition temperature in relation to these three hydrocarbons is brought out in a subsequent section.

Accordingly, comparison of the vapor-phase reactor-tube experiments with spontaneous ignition temperatures in pure oxygen shows that the order in table V is the same for both types of experiments. No reversal of the order is noted with the other compounds listed whose spontaneous ignition temperatures were found using air. The wide spread in spontaneous-ignition-temperature values reduces this possibility. This is not to say an inversion in order could not occur with these compounds. Changes in other variables such as surface-volume ratio of the ignition chamber or pressure, as well as in hydrocarbon-oxygen ratio, may effect such a reversal.

The apparently anomalous behavior of paraffins and olefins as reflected in their respective spontaneous ignition temperatures is worthy of note. Whereas, in the low-temperature regions, the olefins have higher spontaneous ignition temperatures than the corresponding paraffins, the reverse is true at elevated temperatures (ref. 6). This phenomenon emphasizes the importance of physical variables.

Generally, the ease of ignition increases with the length of uninterrupted methylene chain. A notable exception is methylcyclohexane. Although it is isomeric with n-heptane and both have a chain of five uninterrupted methylene groups, methylcyclohexane has a spontaneous ignition temperature of 323° C, or 73° higher than that of n-heptane.

Reaction-tube experiments under similar conditions (compare runs 10 and 8, table V) also show this large difference. One reason for this greater resistance of methylcyclohexane is the relatively greater strength of the strainless, cyclic carbon skeleton compared with that of the straight-chain configuration. Schalla and McDonald (ref. 7) report the carbon-carbon bond strength for cyclohexane and hexane to be 80 and 67 kcal/mole, respectively. By analogy, methylcyclohexane has a greater C-C bond strength than n-heptane (69 kcal/mole). Hence, a main reaction in the oxidation process, the scission of a C-C bond on the decomposition of an alkoxy free radical (ref. 8)

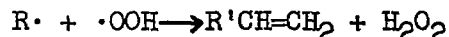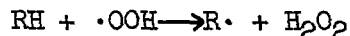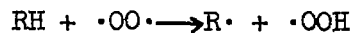$$RO \cdot \longrightarrow R' \cdot + R_2''CO$$
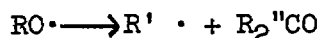
would occur with more difficulty in the cyclic structure than in the straight-chain one. Similarly, the C-H bonds in the cyclic methylene groups are stronger than those of n-heptane (ref. 9) and more resistant to initiation reactions. Although the tertiary radical produced by hydrogen abstraction from methylcyclohexane would be more stable than the secondary radicals from paraffins, the relative inertness of methylcyclohexane is more plausibly related to its cyclic structure and to the absence of selectivity of tertiary attack to reaction temperature. A second factor is the steric influence of the methyl group. Even though the methyl group will be found preponderantly on an equatorial bond in methylcyclohexane, it will still hinder oxygen attack on neighboring hydrogen atoms.

In 3-heptene there are only three uninterrupted methylene groups and a central double bond; these structural features increase its spontaneous ignition temperature 44° C over that of n-heptane (250° C). Yet, the cyclic methylcyclohexane is more resistant to oxidation than this olefin having the same number of carbon atoms. Toluene has a spontaneous ignition temperature of 635° C and is the most stable structure toward oxidation of the series. It is resistant to oxidative degradation at 550° C and 0.16-second contact time in the 1/16-inch-inside-diameter reactor tube. This is typical for aromatic compounds. The fact that the spontaneous ignition temperature of toluene is 10° C lower than that of benzene may be partly attributed to the methyl hydrogens. At these temperatures the 1° hydrogens are more readily attacked by oxygen and contribute to the degradation of toluene. In addition, pyrolysis can more easily occur between the methyl and ring carbons than between two ring carbons as in benzene.

In the initial steps of oxidation of hydrocarbons at low temperatures ($<300^\circ$ C), for example, 3-heptene and n-heptane, organic peroxides are formed in large amounts. Because of the relative stability of the alkylperoxy radicals at these temperatures, they remain intact long enough to abstract a hydrogen atom and form the alkyl hydroperoxide

$$ROO \cdot + RH \longrightarrow ROOH + R \cdot$$
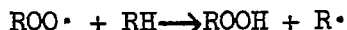
At higher temperatures ($>400^\circ$ C) the first products formed are H_2O_2 and olefins. Here, the concentration of the active oxygen diradical $\cdot OO\cdot$ and the active $\cdot OOH$ radical make the following initiation steps predominant:

$$RH + \cdot OO\cdot \longrightarrow R\cdot + \cdot OOH$$

$$RH + \cdot OOH \longrightarrow R\cdot + H_2O_2$$

$$R\cdot + \cdot OOH \longrightarrow R'CH=CH_2 + H_2O_2$$

For the hydrocarbons tested, the quantity of H_2O_2 in the product exceeds that of ROOH as the oxidation proceeds. The ROOH decomposes rather rapidly as follows:

$$ROOH \longrightarrow RO\cdot + \cdot OH$$

while the more stable H_2O_2 (ref. 10) decomposes more slowly. As the extent of oxidation increases, carbonyl compounds are found in large quantities.

From the data in the tables it is evident that the order of decreasing resistance to both spontaneous ignition and preflame controlled vapor-phase oxidation of the hydrocarbon structures tested is aromatic > branched > cyclic > straight-chain olefin > straight-chain paraffin. Since the spontaneous-ignition-temperature values for these hydrocarbons can be correlated with the vapor-phase oxidation and the environmental conditions are quite similar in both cases, it is probable that the oxidation phenomena occurring are the same.

Effect of Surface-Volume Ratio

In the vapor-phase oxidation of organic compounds, the extent of reaction is greatly dependent upon conditions favorable to free-radical chain branching. Competing with chain-branching reactions are chain-breaking reactions in which free-radical chains are terminated. Termination occurs when a free radical loses or distributes part of its energy

upon collision at a surface with another free radical. Hence, the extent of vapor-phase oxidation can be reduced by increasing the amount of surface area. The amount of internal surface in small-diameter reactors is high relative to the volume of gas flowing through the tube, and the control which a high surface-volume ratio makes possible permits high-temperature reactions (at least 1,000° C) which are otherwise not feasible. An example of the effect of the surface-volume (S/V) ratio is illustrated by the oxidation of isooctane at 550° C and 0.24 second (ref. 3); when a 1/16-inch-inside-diameter reactor tube was replaced by a 1/4-inch-inside-diameter tube, explosive reactions occurred.

Many of the discrepancies in the reported spontaneous-ignition-temperature values of a given compound are probably caused by the difference in surface-volume ratios of the diverse types of ignition vessels used. For example, the spontaneous ignition temperature of benzene has been reported as 645°, 592°, 582°, and 562° C by Frank and Blackham (ref. 1), Jackson (ref. 11), Thompson (ref. 12), and Zabetakis, Furno, and Jones (ref. 13), respectively. In all cases air was used and the air-flow rate was zero except for the 645° C spontaneous-ignition-temperature value which was obtained at 125-cc/min air flow; at 25 cc/min the spontaneous ignition temperature decreased only 6°. Calculation of the surface-volume ratio was made from the description of each of the various vessels used; these are shown in the following table:

Reference	Vessel size, cc	Vessel shape	Material	S/V, cm^{-1}	Spontaneous ignition temperature, °C
1	43	Cylinder	Stainless steel	1.55	645
11	125	[a]Erlenmeyer flask	Pyrex	1.14	592
12	150	[a]Erlenmeyer flask	Pyrex	1.08	582
13	200	[a]Erlenmeyer flask	Quartz	0.98	562

[a]S and V calculations made by assuming flask a right circular cone; V calculation checks well with experiment.

Frank and Blackham reported that the material from which the ignition chamber is constructed has little effect upon the spontaneous ignition temperature (ref. 1) at temperatures below 290° C but, above this temperature, the effect may become pronounced for metals. The Pyrex vessels (refs. 11 and 12) show that factors other than material of construction

are influential. Figure 1 shows a plot of the spontaneous ignition
temperatures of benzene, toluene, isooctane, n-heptane, and n-hexadecane
against the S/V ratio of the ignition vessel in which they were
obtained. Each of the investigators found the same order of ignition
for the five hydrocarbons, although the values were displaced on the
temperature scale. The curves obtained are linear on this graph and
suggest straight-line proportionality between the surface-volume ratio
and spontaneous ignition temperature. This cannot be the case, however,
over the entire range, since the physical limitations of the surface
disappear at very low S/V ratios and cease to play an important role
at higher S/V ratios where the activation of oxygen and hydrocarbon at
high temperatures overshadows the chain-breaking effect of the surface.
If the S/V ratios are varied over a much wider range than that shown
in figure 1, the corresponding change in spontaneous ignition temperature
could reasonably be represented by figure 2. As the S/V ratio approaches
zero, the slope of these S-shaped curves approaches zero also, and essen-
tially parallel lines are secured. Here, the chemical structure of the
hydrocarbon in the fuel-air mixtures is dominant in determining the spon-
taneous ignition temperature, and the absolute minimum spontaneous igni-
tion temperature of a hydrocarbon would most reasonably be found in this
region. It must be remembered that reducing the S/V ratio is not the
only factor leading to lower spontaneous ignition temperatures but that,
by increasing the percentage of oxygen in the mixture from 20 percent
(air) to 100 percent and by employing pressures greater than atmospheric,
the whole family of curves in figure 2 would be shifted to a lower tem-
perature scale. These additional factors will be discussed in more detail
in later sections, but it is noted that the lowest spontaneous-ignition-
temperature values obtainable for a compound (absolute minimum spontaneous
ignition temperatures) will be approached when the S/V ratio approaches
zero, the percent of oxygen approaches 100, and higher-than-atmospheric
pressures are employed. A determination of the absolute minimum spontan-
eous ignition temperatures possibly may be of value in determining bond
energies.

As the S/V ratio becomes very large, the chain-breaking reactions
on the vessel surface increase. When temperatures are reached at which
pyrolysis of the hydrocarbon occurs and the oxygen molecule is energetic
enough to attack any type of C-H bond indiscriminantly, the quenching
caused by chain breaking becomes ineffective.

The extended curves in figure 2 are S-shaped. The interpretation of
the S-shape (ref. 14) is that the steeper slope near the center of such a
curve is caused by the fading out of the low-temperature mechanism of
oxidation before the high-temperature mechanism is fully operative. In
figure 2 the lower temperature S-shaped curves are displaced to higher
S/V ratios, indicating that the low-temperature mechanism (and, hence,
ignition) can be prohibited altogether at higher S/V ratios. This is

illustrated as follows: n-heptane ignites at 244° C (at 25-cc/min air flow) in a 43-cubic-centimeter cup (ref. 1), S/V = 1.55, and exhibits cool flames at 270° C in a 1.7-centimeter-diameter tube (ref. 15), S/V = 2.3, but oxidizes without flame ignition at temperatures of at least 450° C in a 1.16-inch-inside-diameter tube (ref. 2), S/V = 25.3.

Slopes of the benzene, toluene, and isooctane curves in figure 1 are steeper than those of n-heptane and n-hexadecane. At higher temperatures the activity and energy transfer capacity at a surface are greater than at low temperatures and, therefore, the number of effective quenching collisions will also be greater. In the low-temperature ignition region where the surface-volume effect is not nearly so pronounced, the oxidation mechanism depends upon a critical concentration of alkyl hydroperoxides for ignition (ref. 16). Fewer deactivating collisions at the wall occur at this temperature and the peroxide builds up to the critical concentration. This is evidenced by data in numerous papers showing that the longer time lag accompanies low-temperature spontaneous ignition (refs. 1, 5, and 17).

A further demonstration of the S/V effect is shown in figure 3. Spontaneous ignition temperatures of mixtures of various compositions of n-heptane and isooctane are plotted, and the characteristic S-shaped curves are obtained. In all cases the large cup size gave lower spontaneous ignition temperatures. The respective S/V ratios are 1.55 (43-cubic-centimeter cup) and 0.98 (200-cubic-centimeter flask) and correlations agree well with the observed spontaneous-ignition-temperature behavior.

In all three curves of figure 3 the rate of change in spontaneous ignition temperature is much more pronounced in going from a 50:50 composition of n-heptane and isooctane to a 30:70 composition than elsewhere on the curves. It was of interest to determine whether the spontaneous-ignition-temperature behavior would be reflected in the nature and yield of oxidation products in reactor-tube oxidations. Table VI shows the results of runs made on 50:50 and 30:70 mixtures (by volume) at 500° C and 0.04 second in the 1/16-inch-inside-diameter tube, along with results obtained using pure n-heptane and isooctane (at 550° C) reported previously (ref. 2). As expected, runs on the mixtures (runs 2 and 3) show product yields intermediate between those of the pure components. Carbonyl formation predominates in both runs. If it is assumed that the oxidation of isooctane contributes little to the oxidized material found and that the oxidation products stem largely from n-heptane degradation, then the yields may be adjusted to represent only n-heptane by multiplying the values for run 2 by a factor of 2 and those for run 3 by a factor of 10/3. The calculations show that the adjusted yields are less than one-half those obtained with pure n-heptane; aldehydes and acids seem to be especially
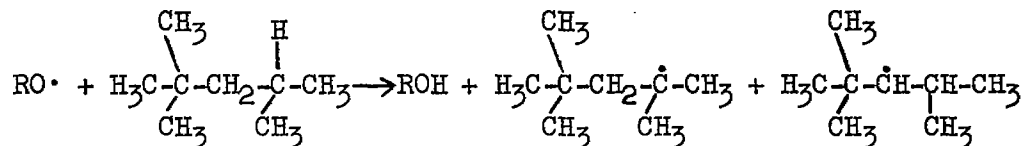
affected. This decrease may be due to dilution of n-heptane by the iso-
octane gas in the reactor, but the accompanying increased stoichiometry
would tend to offset this. Therefore, isooctane cannot be assumed inert
in this environment. Although the oxygen attack on isooctane would be
slight, attack by active free radicals generated from heptane oxidation
might be appreciable. Isooctane has one tertiary (3°) hydrogen and two
secondary (2^O) hydrogens which may be easily abstracted by any initial
free radical formed from heptane. The resulting isooctyl free radical
would be relatively stable. This chain transfer will reduce the amount
of initial products, such as H_2O_2 and olefins. According to reference 7
the alkylperoxy radical and alkyl hydroperoxide decompose to the alkoxy
radical as follows:

$$ROO\cdot \xrightarrow{R\cdot} ROOR \longrightarrow 2RO\cdot$$

$$2ROO\cdot \longrightarrow 2RO\cdot + O_2$$

$$ROOH \longrightarrow RO\cdot + \cdot OH$$
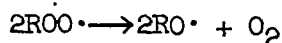
The alkoxy radical decomposes to carbonyl compounds as follows:

$$RO \longrightarrow R'\cdot + R_2''CO$$
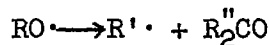
where $R',R'' = H$ or alkyl and $R =$ alkyl. Reaction of the alkoxy radical
with a 3° or 2^O hydrogen would cause the following chain transfer:

$$RO\cdot + H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_3 \longrightarrow ROH + H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2-\overset{\displaystyle\cdot}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_3 + H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-\overset{\displaystyle\cdot}{C}H-\overset{\overset{\displaystyle}{}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}H-CH_3$$

This would account for the small amount of carbonyl formed. In comparison
with pure isooctane, the 30:70 mixture is still quite reactive and exhibits
low-temperature oxidation, probably owing to the decreased hydrocarbon-
oxygen ratio. A similar behavior was noted by Walcutt, Mason, and Rifken

(ref. 15) in preflame oxidation reactions in an engine. The knock resistance of n-heptane - isooctane mixtures increased linearly from 0 to about 70 percent isooctane and then increased markedly.

Effect of Hydrocarbon-Oxygen Ratio on

Spontaneous Ignition Temperatures

It is well known that the composition of a combustible mixture is a critical factor in any oxidation process, especially spontaneous ignition. Numerous data in the literature show flammability limits for various hydrocarbon-air or hydrocarbon-oxygen mixtures ranging on both sides of stoichiometry. Such limits can roughly be represented by figure 4 (ref. 18). In the present spontaneous-ignition-temperature studies, air was used and the variables involved in obtaining the optimum oxygen-fuel mixtures for ignition were air-flow rate, charge size, molecular weight, and rate of vaporization of sample.

As noted previously, the spontaneous-ignition-temperature determinations made in this laboratory were in either stagnant or flowing air. Air-flow rates were varied from zero to 125 cc/min. Flowing air more closely simulates actual aircraft flying conditions and, therefore, most spontaneous ignition temperatures were reported for 125 cc/min. In general, the spontaneous-ignition-temperature values are lower for stagnant air conditions (zero air flow). Some notable exceptions are the diesters (ref. 6), the organic phosphorous esters (ref. 19), and various blends of commercial oils with hydrogenated polyisobutylene (refs. 14 and 19). Zero air flow leads to the most readily combustible mixtures in this apparatus since the critical intermediates can reach the concentration necessary for chain branching and ignition. Also, longer time lags before ignition are observed. Higher air-flow rates tend to sweep out such intermediates as the ignition proceeds and the critical concentration is not so readily attained. Hence, with higher air flows the spontaneous ignition temperature will necessarily be at a somewhat higher temperature where reaction rates are greater.

The charge size was varied at a constant air-flow rate as the temperature was changed. It was observed that either too little or too much fuel at a given temperature and air-flow rate resulted in no ignition. As shown in figure 4, the former type of mixture is too lean and the latter, too rich. In the high-temperature region the charge size necessary for ignition is always small. Apparently, greater oxygen activity and concurrent pyrolysis diminish the need for large hydrocarbon concentrations. Upon decreasing the temperature the required charge size for an ignition is increased. Although flammability limits for spontaneous-ignition phenomena have not been clearly defined, Di Piazza, Gerstein,

and Weast (ref. 20) note maximum flammability for various hydrocarbons in air (at different pressures) to be about 120 percent stoichiometry (HC/O_2). In most cases, this stoichiometry is exceeded in the 43-cubic-centimeter ignition chamber, even at minimum charge sizes.

It was found that, with viscous and high-molecular-weight oils and with compounds having low vapor pressures, the rate of vaporization greatly influences the spontaneous ignition temperature. Employing spray-injection procedures, these spontaneous ignition temperatures were lowered, often as much as 100^6 C. This, again, is evidence of the need for attaining the most favorable hydrocarbon-oxygen (HC/O_2) ratio in order for ignition to occur, especially at low temperatures. Figure 3 shows the effect on spontaneous ignition temperature of increased vaporization rate and increased HC/O_2 ratio for n-heptane - isooctane blends. The spray method gives considerably lower values of spontaneous ignition temperature than the drop method. The same figure shows that the HC/O_2 ratio obtained in the larger cup (200 cubic centimeters or five times the volume of the smaller cup, ref. 13) is more favorable for ignition. Here, the lower HC/O_2 ratio and the lower S/V ratio combine to give a still lower spontaneous-ignition-temperature curve for the blends.

Air was used as the source of oxygen in all the spontaneous-ignition-temperature determinations in order to approach more closely actual flying conditions, and the charge size was varied. For a constant charge the ignition temperature has been shown to be dependent upon the percent oxygen used (ref. 5). Comparing these reported ignition temperatures for 2,2-dimethylbutane, isooctane, and 2,3-dimethylbutane in air (20 percent O_2) with those obtained in the present work (see table below), it is noted that the order of decreasing spontaneous ignition temperature is the same in both cases

Compound	Spontaneous ignition temperature, °C		
	Air	Air (a)	Oxygen (a)
2,2-Dimethylbutane	524	580	310
Isooctane	515	565 ·	318
2,3-Dimethylbutane	497	540	328

ᵃValues approximated from graph (ref. 5).

The results reported in reference 5 are correspondingly higher because of the larger S/V ratio of the ignition vessel (21-cubic-centimeter cylindrical cup compared with a 43-cubic-centimeter cup). However, upon increasing the percentage of oxygen flowing through the chamber (at 25 cc/min), the spontaneous ignition temperature is gradually reduced as more ideal stoichiometries are reached. At 100 percent oxygen, positive

ignition for 2,2-dimethylbutane and cool-flame ignition points for iso-
octane and 2,3-dimethylbutane were reported (see table on preceding page).
Positive flames for the latter two seem reasonable if the charge size were
varied, provided that the mixture at 100 percent oxygen was not already
the most ideal. Since ignition of these highly branched paraffins was
obtained only with the most favorable HC/O_2 ratios, the absence of spon-
taneous ignition at low temperatures using air is understandable. It will
be noted that the order of spontaneous-ignition-temperature values is
reversed at lower HC/O_2 ratios. In table V the various hydrocarbons are
listed in order of decreasing values of spontaneous ignition temperatures.
If, however the listing were according to the product yield from these
three hydrocarbons, the order would be reversed. This reversal is very
likely due to the change in stoichiometry from less than 1 (in air) in
spontaneous-ignition-temperature experiments to unity in flowing reactor-
tube experiments.

A possible explanation for the differences in reactivity at various
temperatures and HC/O_2 ratios may be the differing susceptibilities to
oxidation and pyrolysis, as suggested by Cullis and Hinshelwood (ref. 21).
At low temperatures (approximately 260° C) where selective oxidation occurs,
2,2-dimethylbutane is 12 times more reactive than the 2,3-isomer to oxida-
tion. This is probably caused by the reactivity of the methylene group
in the 2,2-isomer and to the steric shielding of the two 3° H atoms by
methyl groups in the 2,3-isomer (Fisher-Hirschfelder models). However, at
higher temperatures and lower oxygen concentration, the greater pyrolytic-
reaction rates overshadow oxidation rates and the more highly branched
2,3-dimethylbutane is more easily pyrolyzed.

Effect of Other Variables on Spontaneous

Ignition Temperature

Increasing the pressure of the gas system being ignited is another
means of reducing the spontaneous ignition temperature of a compound.
All of the spontaneous-ignition-temperature values reported herein were
determined at atmospheric pressure. However, when n-heptane and isooc-
tane were separately placed under pressures up to 10 atmospheres in an
explosion bomb (ref. 22), they spontaneously ignited at temperatures
lower than had been previously observed, namely, at 230° and 290° C,
respectively. Thus, under extreme conditions isooctane ignites spon-
taneously by positive flame in the low-temperature region. The curves
of spontaneous ignition temperature versus pressure show the character-
istic S-shape and cool flames in the 300° to 400° C range for both com-
pounds. This nonignition zone for isooctane provides further evidence
for the validity of the two mechanisms of oxidation, one for high tem-
peratures and another for low temperatures. At pressures greater than
those noted for minimum values of spontaneous ignition temperature
(1.9 atmospheres for n-heptane and 4.85 atmospheres for isooctane), the
spontaneous ignition temperature is not lowered substantially and the

curve becomes parallel to the pressure axis at a certain temperature
level. These temperature levels for various structures seem significant
and with further study could possibly reveal intimate relationships
between bond energies and relative structural strength of compounds.

Still other variables which affect the spontaneous ignition tem-
perature of a compound are the material of construction of the igni-
tion chamber and its condition, the sample purity, and the molecular
weight of the sample. The differences in spontaneous ignition tempera-
ture due to the use of various materials for ignition chambers were
found to be pronounced at high temperatures and negligible at lower tem-
peratures. It is probable that, at high temperatures, oxide coatings
and flaking at the vessel walls present more surface for chain breaking,
and this greater surface-volume ratio is manifested by a higher spon-
taneous ignition temperature. Naturally, the purity is important. Some
types of impurities may inhibit ignition by terminating free-radical
chains, for example, aryl amines, and others may induce or promote igni-
tion by furnishing additional reactive free radicals, for example, per-
oxides and certain aldehydes. The influence of molecular weight on
spontaneous ignition temperature is due mainly to vaporization rates.
Also, preheating samples which are solids at room temperature and which
must be melted before introduction into the chamber may influence the
spontaneous ignition temperature.

Meaning and Implications of Minimum

Ignition Temperature

A great deal of data has appeared in the literature on the behavior
of hydrocarbons and other organic compounds to spontaneous ignition.
Various terms such as minimum ignition point, spontaneous ignition tem-
perature, and spontaneous ignition point have been used to indicate the
lowest temperature at which a positive flame, cool flame, or smoke pulse
will appear under existing conditions. Unfortunately, there are wide
discrepancies in the results reported for the spontaneous ignition tem-
perature of any particular compound. It is recognized that these differ-
ences arise because the ignition apparatus and the conditions employed
are not at all standardized. For the most part they are varied by each
investigator to give the greatest amount of data pertaining to a specific
problem of spontaneous ignition or else to study closely only a few vari-
ables involved. While this type of information is highly useful and
desirable, it does not always permit close correlation with other work
of the same nature. Hence, an overall picture of the physical and chem-
ical conditions which affect and are important in spontaneous-ignition
behavior has been slow in developing. It has often been suggested, for
example, that there is a specific lowest temperature at which a certain
combustible will ignite spontaneously, that is, an "intrinsic"

spontaneous ignition point. Even though there is theoretical significance
to this supposition, the so-called minimum spontaneous ignition tempera-
tures reported in the literature are minimum for the particular apparatus
only and in most cases can be reduced by changing one or more variables.

The chief variables affecting the ignition behavior of a compound
are temperature, S/V ratio, HC/O$_2$ ratio, pressure, ignition-vessel
material, and sample purity. While each of these variables has been
studied separately or in groups, investigations of the oxidation phenomena
in which all these essential variables are considered and related have not
been attempted. If one compound, isooctane, for example, were studied
extensively using a complete set of conditions, it would then be possible
to construct three-dimensional solid models with spontaneous ignition tem-
perature, S/V ratio, and pressure as the coordinates. Such a model is
shown in figure 6. The highest spontaneous ignition temperatures would
occur at high S/V ratios and low pressures and the lowest spontaneous
ignition temperatures, at low S/V ratios and high pressures. Interme-
diate spontaneous-ignition-temperature values would occur at the other
extremes of low S/V ratio and low pressure and high S/V ratio and
high pressure. The fold in the surface represents the nonignition zone
in going from high to low spontaneous ignition temperatures. A number of
surfaces of this type could be constructed for HC/O$_2$ ratios on either side
of and including stoichiometric mixtures. Certainly it would entail a
vast amount of work to describe all compounds so thoroughly, but the
wealth of information that could be obtained from just a few sets, that
is, using only a few representative compounds and using blends, such as
n-heptane - isooctane mixtures, and plotting spontaneous ignition tempera-
ture, percent composition, and pressure at various HC/O$_2$ ratios, would
probably justify such an effort. The existence of high- or low-temperature
oxidation mechanisms or both for various classes of organic compounds under
a wide range of conditions could be ascertained. The dependence on these
variables of the nonignition zone and cool-flame areas and the relation
of engine knock to these variables could be more clearly outlined. Quali-
tative and quantitative studies of the initial oxidation products at
select points on the surface would add information on actual steps in the
oxidation at high or low temperatures, helping to resolve and describe
the two proposed mechanisms. Besides adding to the fundamental knowledge
of oxidation, such investigations would certainly be useful in engine-
combustion research of various phases, for example, engine knocking and
efficiency, use of additives, and so forth.

From the consideration of how the spontaneous ignition temperature is
influenced by the important variables discussed, it is probable that no
absolute minimum spontaneous ignition temperature for any particular com-
pound has been reported. It is altogether possible that the absolute
minimum spontaneous ignition temperature can only be approached and a

theoretical value found by extrapolation. To obtain the minimum spontaneous-ignition-temperature values, conditions of low S/V ratio, higher-than-atmospheric pressures, and optimum HC/O_2 ratio are necessary.

CONCLUSIONS

From a comparison of the spontaneous ignition temperatures of eight representative hydrocarbons with their preflame oxidation behavior in a flowing system and from the effect of environmental conditions on these spontaneous-ignition-temperature values, the following conclusions may be drawn:

1. Reducing the stoichiometry of a hydrocarbon-oxygen gas mixture to less than unity decreases the extent of oxidation, other conditions remaining unchanged.

2. The extent of oxidation of methylcyclohexane in a flowing system varies with temperature in a manner characteristic of compounds showing a nonignition zone during spontaneous-ignition-temperature determinations.

3. Spontaneous ignition temperatures correlate quite well with the extent of vapor-phase oxidation in a flowing system, an indication that the oxidation phenomena accompanying these two modes of hydrocarbon oxidation are similar.

4. Cyclic hydrocarbons have greater resistance to preflame oxidation than both the straight-chain olefins and paraffins with the same number of carbon atoms. The order of decreasing resistance for the hydrocarbon structures tested is aromatic > branched paraffin > cyclic paraffin > straight-chain olefin > straight-chain paraffin.

5. In the various types of apparatus employed, the spontaneous ignition temperature of a compound varies linearly and directly with the surface-volume (S/V) ratio of the ignition chamber. Use can be made of high surface-volume ratios to control oxidation reactions.

6. The spontaneous ignition temperature of a compound is intimately dependent upon the stoichiometry (fuel-oxygen ratio) of the gaseous combustible mixture; this dependence decreases at elevated temperatures.

7. Both high- and low-temperature oxidation of highly branched hydrocarbons can be obtained by changing one or more of the variables, S/V ratio, HC/O_2 ratio, and pressure. Observations of the effects of these variables indicate that this would be true with any hydrocarbon type.

8. The absolute minimum spontaneous ignition temperature of a compound is a theoretical value, and none reported in the literature can be regarded as the lowest spontaneous ignition temperature. The conditions necessary in approaching the lowest spontaneous-ignition-temperature value are low S/V ratio, higher-than-atmospheric pressure, and optimum fuel-oxygen ratio.

9. Valuable fundamental information on preflame oxidation variables, nonignition zones, high- and low-temperature oxidation mechanisms, and minimum values of spontaneous ignition temperature may be obtained by constructing surface models with spontaneous ignition temperature, S/V ratio, and pressure as coordinates at various fuel-oxygen ratios for a number of representative hydrocarbon types. Similar information on blends could be secured with spontaneous ignition temperature, percent composition, and pressure as coordinates at various fuel-oxygen ratios.

University of Cincinnati,
    Cincinnati, Ohio, January 26, 1955.

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    Ignition Temperatures of Combustible Liquids and Gases. Analytical
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TABLE I.- OXIDATION OF TOLUENE

Reaction mixture number	1	2
Conditions:		
Fraction of stoichiometry	1.0	1.0
Temperature, °C	550	550
Contact time, sec	0.16	0.64
Product analysis:		
Hydrogen peroxide, millimole/mole toluene charged	0.6	1.7
Organic peroxides, millimole/mole toluene charged	None	0.1
Total carbonyl, millimole/mole toluene charged	Trace	Trace
Aldehydes, millimole/mole toluene charged	Trace	Trace
Acids, millimole/mole toluene charged	None	1.4

TABLE II.- OXIDATION OF METHYLCYCLOHEXANE FOR VARIOUS STOICHIOMETRIES

Reaction mixture number	1	2	1	1	2	3	4	5	1
Conditions:									
Fraction of stoichiometry	1.0	1.0	0.2	0.1	0.1	0.1	0.1	0.1	0.05
Temperature, °C	350	400	500	350	400	450	500	550	550
Contact time, sec	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16
Analysis:									
Hydrogen peroxide, millimole/mole methylcyclohexane charged	None	120	104	2.3	56	27	24	44	24
Organic peroxides, millimole/mole methylcyclohexane charged	None	None	None		None	None	None	None	None
Acids, millimole/mole methylcyclohexane charged	None	54	29	0.8	26	7.9	2.4	5	14
Olefins									
Qualitative test $\left(Br_2 \text{ in } CCl_4\right)$ . . .	-	+	+	-	+	+	+	+	+
[a]Relative amount $\left(\Delta n_D^{23}\right)$	0	0.0063	0.0053	0	0.0038	0.0012	0.0009	0.0025	0.0013

[a]Increase in refractive index of product.

TABLE III.- EFFECT OF STOICHIOMETRY AND TEMPERATURE

ON OXIDATION OF METHYLCYCLOHEXANE

[Contact time, 0.16 sec]

Stoichiometry	Millimoles of hydrogen peroxide per mole of methylcyclohexane charged for temperatures of -				
	350° C	400° C	450° C	500° C	550° C
1.0	None	120			
.2				104	
.1	2.3	56	27	24	44
.05					24

Stoichiometry	Millimoles of acid per mole of methylcyclohexane charged for temperatures of -				
	350° C	400° C	450° C	500° C	550° C
1.0	None	54			
.2				29	
.1	0.8	26	7.9	2.4	5
.05					14

Stoichiometry	Relative amount of olefins as measured by refractive index of product, $\Delta n_D^{23} \times 10^4$, for temperatures of -				
	350° C	400° C	450° C	500° C	550° C
1.0	0	63			
.2				53	
.1	0	38	12	9	25
.05					13

TABLE IV.- SPONTANEOUS IGNITION TEMPERATURES

Compound	Spontaneous ignition temperatures, °C, at 125 cc/min
Toluene	635
2,2-Dimethylbutane	524
2,2,4-Trimethylpentane (Isooctane)	515
2,3-Dimethylbutane	497
2,2,5-Trimethylhexane	493
Methylcyclohexane	323
3-Heptene	294
n-Heptane	250

TABLE V.- COMPARISON OF SPONTANEOUS IGNITION TEMPERATURES

WITH VAPOR-PHASE OXIDATION BEHAVIOR

Compound	Run number	Spontaneous ignition temperature, °C, at 125 cc/min	Conditions (a)		Product analysis, millimole/mole hydrocarbon					
			Temperature, °C	Contact time, sec	Hydrogen peroxide	Organic peroxide	Olefins	Total carbonyl	Aldehydes (b)	Acids
Toluene	1	635	550	0.16	0.6	None		Trace	Trace	None
[c]2,2-Dimethylbutane	2	524	500	.08	1.2	0.8	3.6	0.73	0.23	0.40
[d]Isooctane	3	515	550	.08	1.6	.16	3.5	1.1	.6	
[c]2,3-Dimethylbutane	4	497	500	.08	.57	.76	2.9	Trace	Trace	None
[d]2,2,5-Trimethylhexane	5	493	550	.08	7.5	4.3	6.1	70	6.8	2.8
	6	493	450	.16	17		13	51	15	7.3
Methylcyclohexane	7	323	400	.16	120	None				54
	8	323	350	.16	None	None				None
[c]3-Heptene	9	294	350	.04	27	4.5		220	110	28
[d]n-Heptane	10	250	350	.04	79	2.1	78		360	60

[a]Stoichiometry hydrocarbon-oxygen compositions, 1:1.

[b]For simplicity, derivative mixture of aldehydes considered to have molecular weight of HCHO derivative (292).

[c]Reference 3.

[d]Reference 2.

TABLE VI.- OXIDATION OF VARIOUS MIXTURES

OF ISOOCTANE AND n-HEPTANE

Reaction mixture number	1	2	3	4
Conditions:				
Percent isooctane by volume	0	50	70	100
Percent n-heptane by volume	100	50	30	0
Fraction of stoichiometry of mixture	1.0	1.0	1.0	1.0
Temperature, $^{\circ}$C	500	500	500	550
Contact time, sec	0.04	0.04	0.04	0.04
Product analysis:				
Hydrogen peroxide, millimole/mole				
hydrocarbon mixture charged	86	19	14	0.51
Other peroxides, millimole/mole				
hydrocarbon mixture charged	1.0	0.2	None	0.05
Olefins, millimole/mole hydrocarbon				
mixture charged	93	[a]13	[a]4.2	0.8
Total carbonyl, millimole/mole				
hydrocarbon mixture charged	None	36	30	Trace
[b]Aldehydes, millimole/mole hydro-				
carbon mixture charged	310	28	18	Trace
Acids, millimole/mole hydrocarbon				
mixture charged	40	8.8	5.6	None

[a]Percent by volume of hydrocarbon residue from chromatographic analysis (ref. 23).

[b]For simplification, molecular weight of the HCHO derivative (292) is used in calculations.
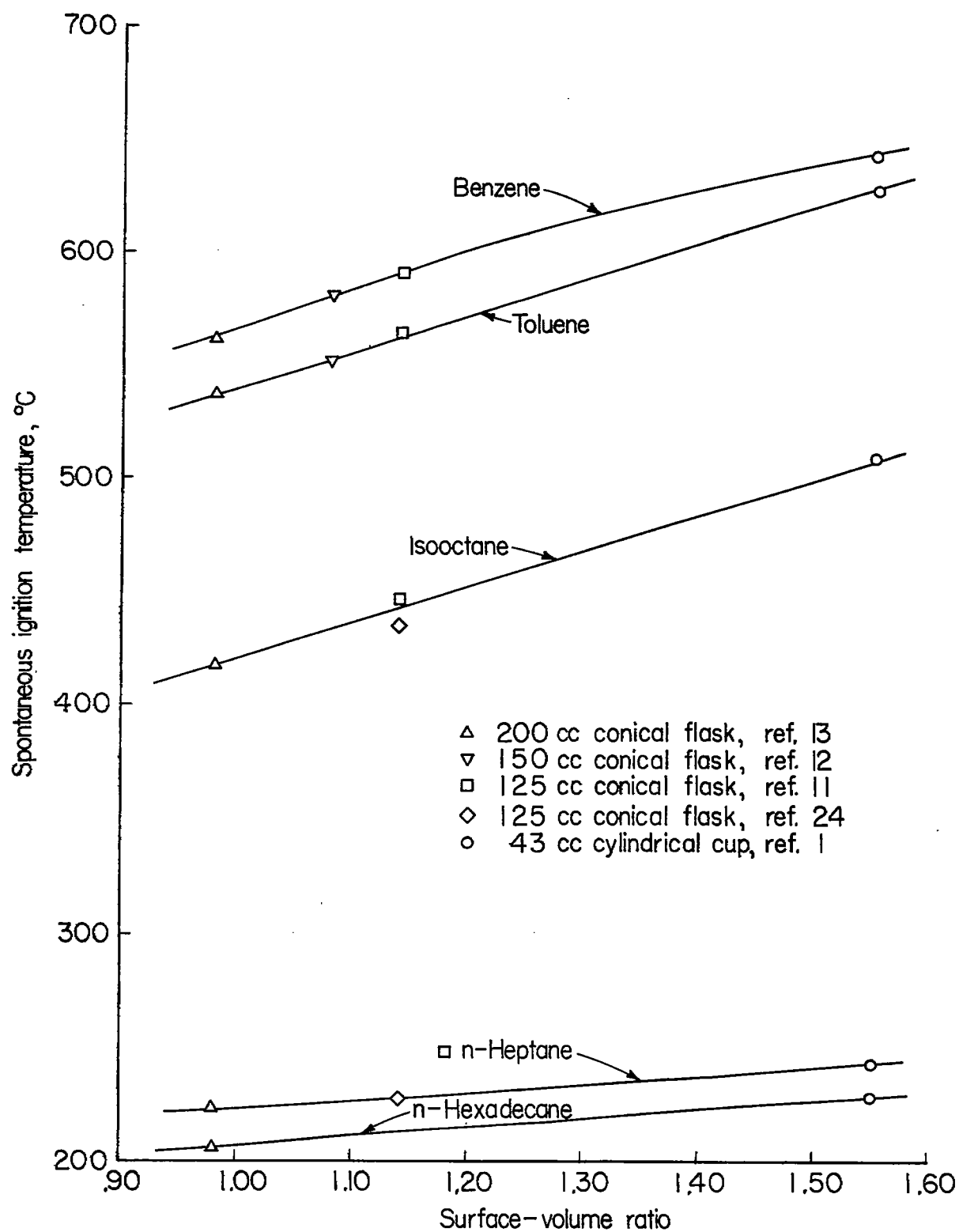
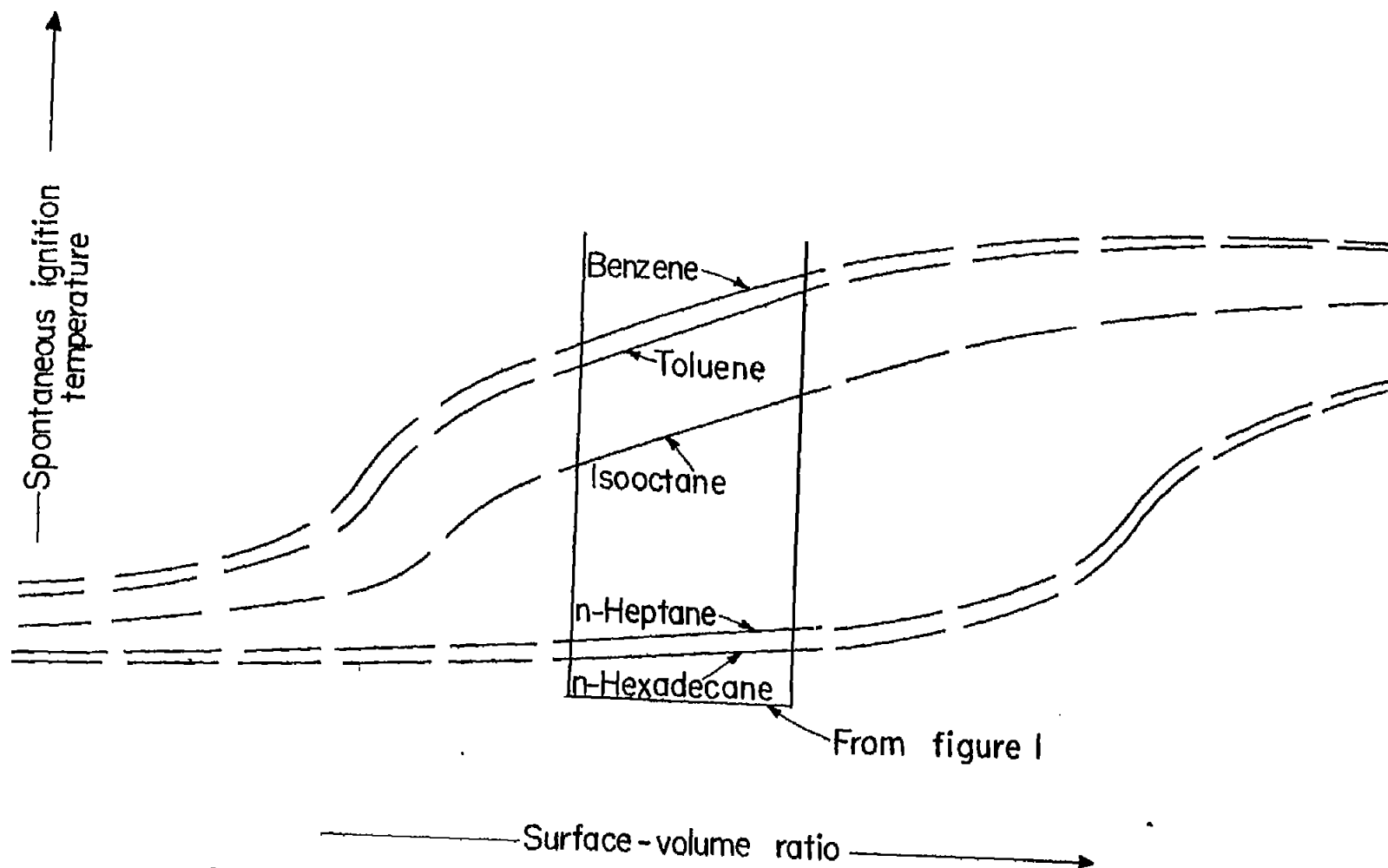Figure 1.- Effect of surface-volume ratio on spontaneous ignition temperature.

Figure 2.- Extended curves showing effect of surface-volume ratio on spontaneous ignition temperature.
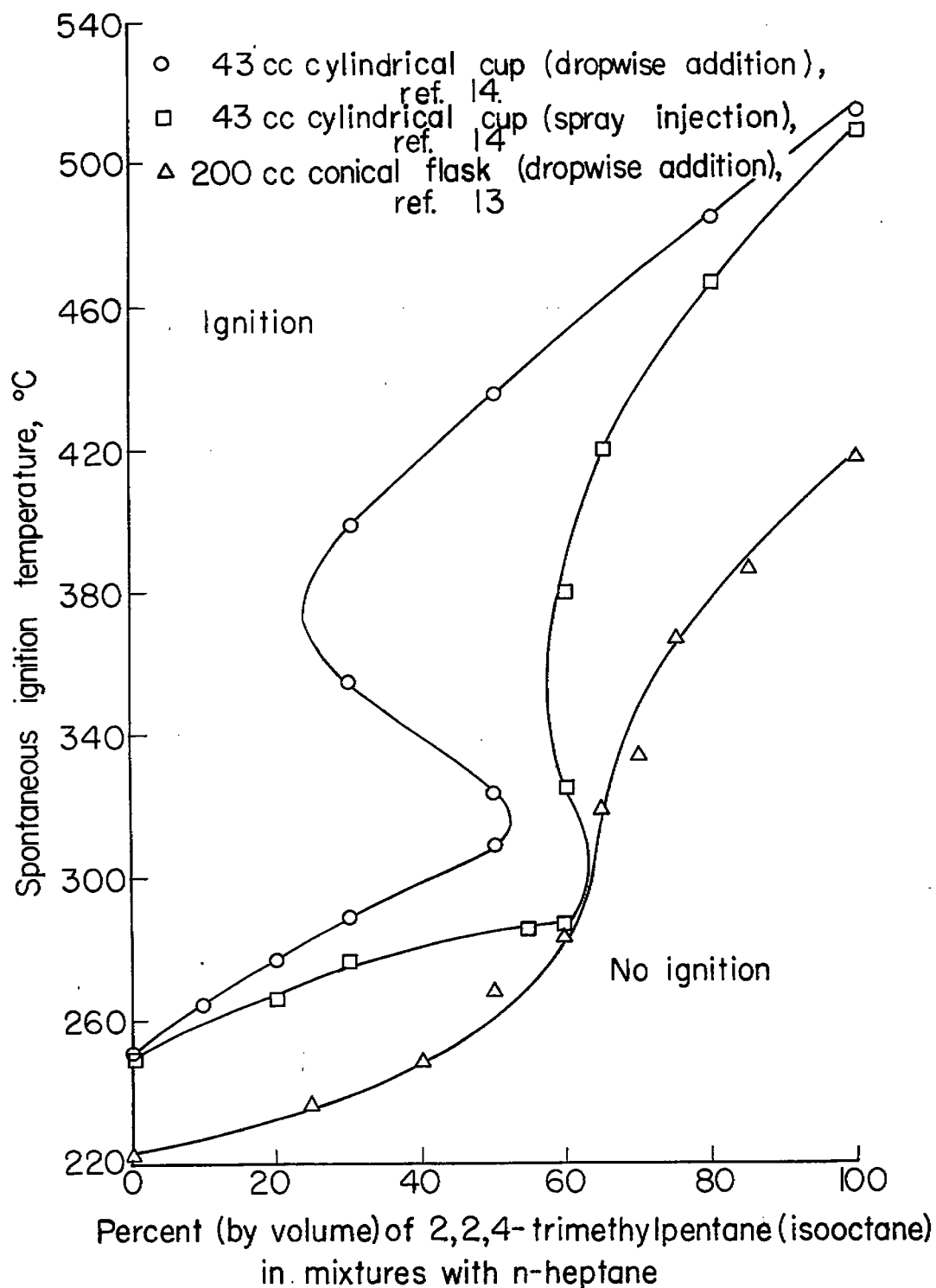
Figure 3.- Effect of surface-volume ratio (vessel size) and hydrocarbon-oxygen ratio (method of hydrocarbon addition) on various 2,2,4-trimethylpentane (isooctane) - n-heptane mixtures.
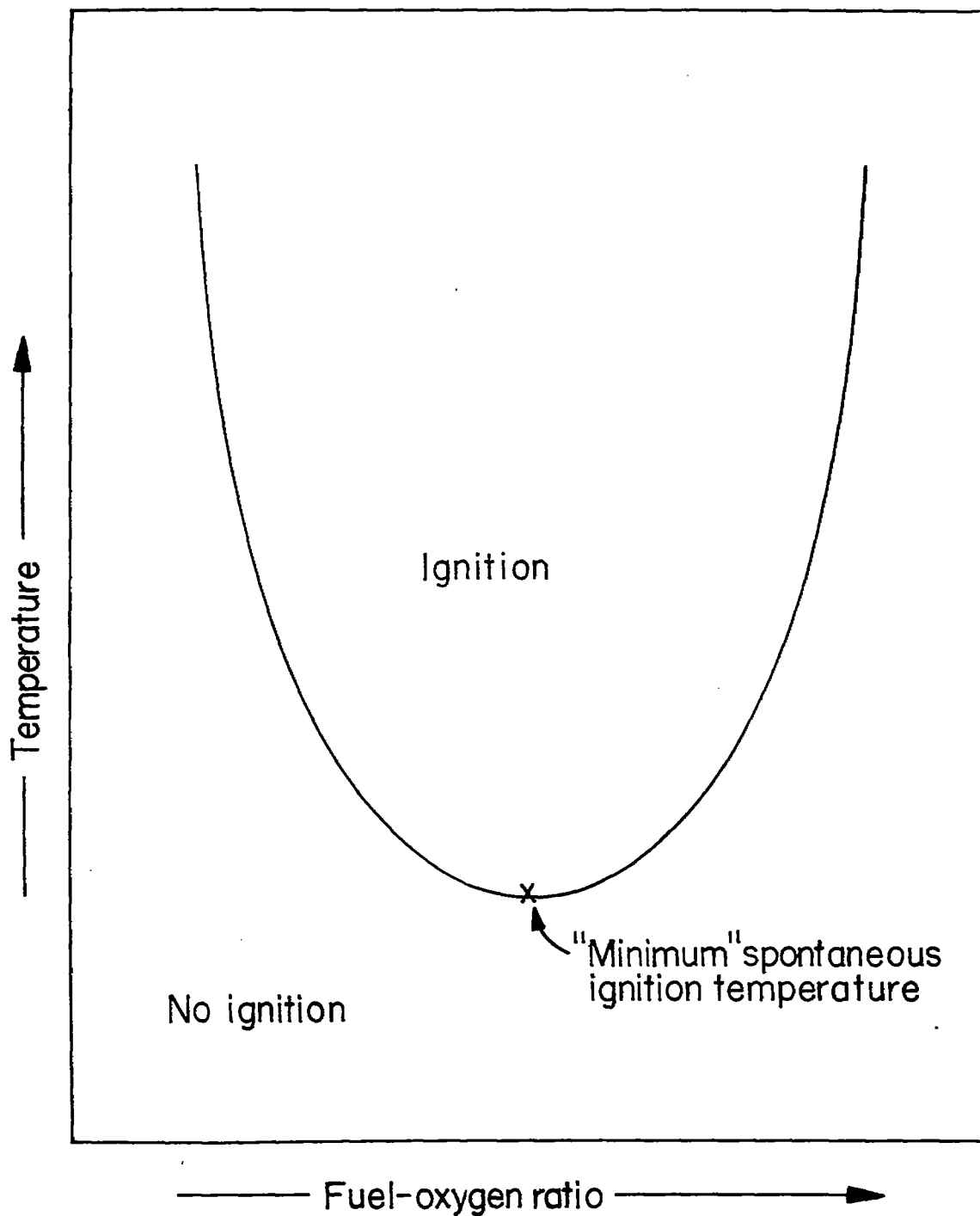
Figure 4.- Typical ignition curve showing effect of fuel-oxygen ratio on
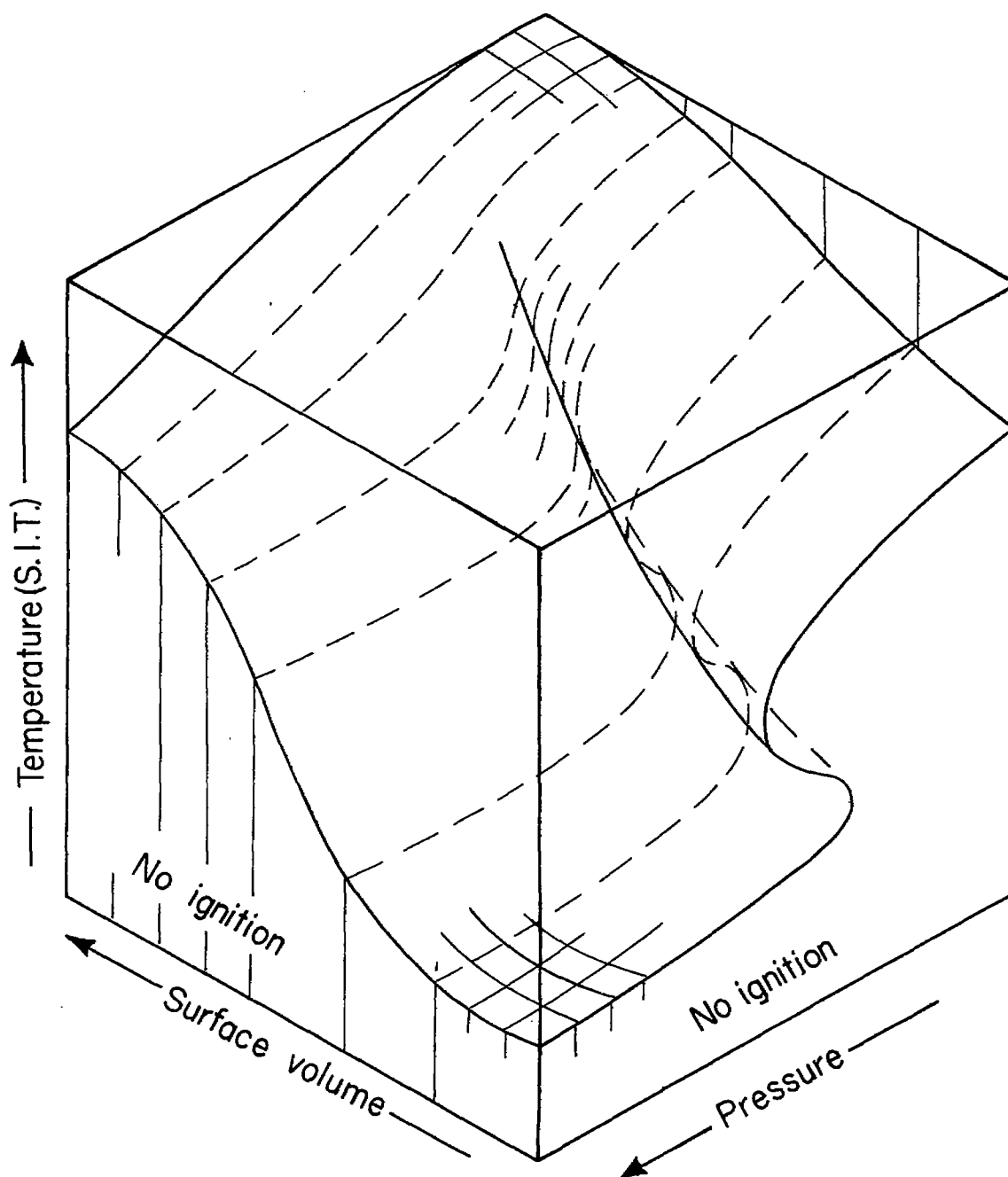spontaneous ignition temperature.

Figure 5.- Typical surface model representing boundary between spontaneous
    ignition and no spontaneous ignition of a hydrocarbon for varying spon-
    taneous ignition temperatures, surface-volume ratios, and pressures.
    Fuel-oxygen $\left(HC/O_2\right)$ ratio constant.